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GLOW DISCHARGE EFFECTS ON POLYETRAFLUOROETHYLENE POLYMERS
INVESTIGATED BY SECONDARY ELECTRON MICROSCOPY AND X-RAY PHOTOELECTRON SPECTROSCOPY

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Abstract
A glow discharge treatment of Polytetrafluoroethylene avoids charging effects and permits observation of the sample in Scanning Electron Spectroscopy: X-ray Photoelectron Spectroscopy has been used to study changes in the surface chemical composition and electronic structure of the polymer produced by this treatment.

Introduction
Studying organic or mineral insulators by means of an electronic probe is very difficult owing to charge build up which occurs under the beam (3, 6, 12). In Scanning Electron Microscopy (SEM), this effect hampers any high magnification observation. On Polytetrafluoroethylene (Teflon, PTFE), this problem can be partly overcome by putting the sample in a glow discharge.

This paper deals with this phenomenon. In order to understand the physical and chemical process induced on the samples by the discharge which leads to better observation conditions, PTFE surface sample were studied in X-ray Photoelectron Spectroscopy (XPS). Impurity metal atoms are deposited on the treated surface and other structural modifications occur which change the surface conductivity.

Experimental
Samples
Technological PTFE (TF 7 synthetized by Dupont de Nemours) was used in the form of 15 mm x 2 mm cylindrical disk samples. Firstly, the samples were cleaned in acetone in an ultrasonic bath. Glow discharges in Argon were generated by a JEOL 111 Fine Coat. The experimental conditions were: vacuum 10⁻¹ torr, current: 4 mA, voltage: 800 V, time 5 to 8 min. To check the spatial resolution some metal coated samples (Au Pd) were also prepared.

Methods
Secondary Electron images were obtained with a JEOL Scanning Electron Microscope JSM 840. The accelerating voltage used for the observations was 1, 2 or 3 keV.

X-ray Photoelectron Spectroscopy was performed in a V.G. Instruments ESCALAB MK II. This instrument is equipped with a non-monochromatized X-ray source.
Fig. 1. S.E. images of PTFE samples.

1a) PTFE-nt - magnification $10^3$.
1b) PTFE-t - magnification $10^3$.
1c) PTFE-m - magnification $10^4$.
1d) PTFE-m - magnification $10^3$.
1e) PTFE-m - magnification $10^4$.

Fig. 2. X-ray photoelectron lines.
2a) PTFE-nt sample.
2b) PTFE-t sample.

Fig. 3. F1s lines for the PTFE-nt and PTFE-t samples.

Fig. 4. C1s lines for the PTFE-nt and PTFE-t samples.
Glow discharge effects on PTFE polymers

(Aluminum Kα, 1486.6 eV). The base pressure is normally around 5 × 10⁻¹¹ Torr. Because of out-gassing effects due to the PTFE samples, the pressure rose to about 10⁻⁹ Torr at the end of the experiment. The analysis chamber is fitted with a 150 mm spherical sector analyzer operating in constant pass energy mode and equal to 50 eV. In this experiment, the energy calibration was made by using the $1f/2, 1s$ X-ray photoelectron line of clean bulk polycrystalline gold.

Results

S.E. images: Three PTFE samples were investigated by means of a scanning electron microscope at a magnification of 10³. The first sample was cleaned in a ultrasonic bath (PTFE-nt), the second one was submitted to a glow discharge (PTFE-t) and last one was coated with metal (PTFE-m). It is interesting to note that the “non-treated” polymer (Fig. 1a) charged up under the electronic probe even at a low accelerating voltage. However, the PTFE-t (Fig. 1b) and the PTFE-m (Fig. 1c) samples present a good imaging contrast and a clear topography. At a higher magnification (10⁴), it was quite impossible to get a useful image on the non-treated polymer (PTFE-nt). On the two other samples (Fig. 1d and 1e), we obtain good details of the surface. The PTFE-t sample shows some morphological surface modifications: etch pits and crosslinking like features.

X-ray photoelectron lines: Owing to the positive charge created by X-ray irradiation (10) a correction of the energy position of the photoelectron and Auger lines is necessary. Comparison with previous work (1, 7) on PTFE led us to choose the value of 690.2 eV for the PTFE-nt sample. This value enabled us to evaluate the $1s$ shift due to the charging of the sample as 7.0 eV for the PTFE-nt and 5.8 eV for the PTFE-t. In the following we will only consider the corrected values of the binding energies.

a) Elemental analysis of the PTFE-nt surface (Fig. 2a) — We note the presence of oxygen ($1s_1$) due to atmospheric contamination and a very small photo-electron line located at 625 eV and probably due to the presence of iodine ($1s_3$) used to fluorinate the compound before polymerization (IF₄). The $1s$ line appears as a convolution of two peaks. If we compare the complete spectrum (Fig. 2a) to that obtained for the PTFE-t sample (Fig. 2b) we observe some modifications: splitting of the $1s$ line shape, and a higher concentration of oxygen. Other photoelectron and Auger lines are found which are due to the presence of metallic atoms (Cu, Fe, Mn, Cr) on the PTFE-t.

b) $1s$ lines (Fig. 3) — For the PTFE-nt sample, we only get a simple $1s$ line at 690.2 eV. On the other hand, the $1s$ line of the PTFE-t reveals a main structure at 689.2 eV which corresponds to the fluorine photoelectron line in PTFE and a second one at lower binding energy (689.2 eV) which can be attributed to metallic fluoride compounds due to deposition of metal atoms (2, 9).

c) $1s$ lines (Fig. 4) — The $1s$ line corresponding to the PTFE-nt sample reveals two distinct structures at 292.4 eV and 288.2 eV which are respectively attributed to the -CF₂- and CF groups in the polymer (2, 8, 11). Photoelectron $1s$ line of the PTFE-t exhibits a less prominent structure at 293.6 eV (-CF₂-) and a new structure at 287.8 eV which can be explained by a presence of a double bond (C=C) in the modified polymer.

Discussion

Two effects can explain the good contrast of the S.E. image made on PTFE-t: low concentration deposit of metallic atoms and partial graphitization of the polymer surface.

The metal atoms were deposited during the short glow discharge and were extracted from the stainless steel surface of the sample holder of the JFC-111. Their concentration is very low (1%) as the line intensity is very weak and as they could not be detected with an Auger microprobe. At this low concentrations, metal atoms cannot produce a conductive surface layer but they can make trapped electron surface sites disappear, leading to a better conductivity.

On the other hand, the energy position, the chemical shifts and the shapes of the photoelectron lines of PTFE (C₁s, F₁s) reveal structural modifications after the glow discharge treatment. Appearance of -C=O groups is correlated to the decrease of -CF₂- and -F- lines. This shows that the glow discharge induced carbon-fluorine bonds to break with the formation of C=C bonds and this partial graphitization leads to reticulation on the PTFE surface (4, 5). This phenomenon has also been observed after much more energetic ion bombardment (+1 keV) (2, 11). The effect is apparent on the S.E. image at high magnification (10⁴).

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Discussion with reviewers

T.J. Shaffner: Could not one deposit gold, 
silver or other metal of choice instead 
of the stainless steel? What properties 
of such a metal would be the most 
desirable?

Authors: The stainless steel was 
accidently deposited during the RF glow 
discharge. It is known that non 
oxidizable metals like gold, platinum or 
non-metallic compounds like graphite 
sputtered onto metal insulator materials 
led to good SEM observations because of 
the disappearance of the superficial 
charging effects.

T.J. Shaffner: How does the time of 
exposure to glow discharge affect the 
apparent conductivity of the PTFE and 
your ability to form images free from 
charging?

Authors: A glow discharge in an inert gas 
is generally used to clean a sample 
surface, but this method applied to 
polymer compounds alters the polymer 
itself because of the temperature 
increase of the sample during the 
treatment. This temperature increase 
generally leads to partial carbonization 
or graphitization of the polymer and in 
this case improves the conductivity.

T.J. Shaffner: The images of Fig. 1d and 
to show that glow discharge has altered 
the surface morphology. Although this 
reduces charging for high magnification 
work, the image one obtains does not 
correctly portray the original surface. 
Does this not invalidate practical 
application of the method for reducing 
charging?

Authors: As the glow discharge alters 
the original surface, it must be used 
carefully to get correct images of the 
surface.

T.J. Shaffner: What is the reason for the etch 
pits and other inhomogeneities after the 
rather short low voltage glow discharge 
treatment?

Authors: We suggest that during the glow 
discharge, inert gas ions interact with 
the atoms of the polymer surface to 
initiate radicals and ions. These species 
rapidly evolve and give backbone 
fragmentations, cross-linking and 
volatile species. These modifications can 
explain the new topography of the 
surface.

R.Holm: What happens to the sample after 
extended treatment or in the case of 
other discharge parameters?

Authors: We did not modify the parameters 
of the surface treatment of the sample, 
as our aim was only to understand the 
modifications of the SEM imaging.